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EP 0125781 A1 US 4557898 A US 4547306 A

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(54) Thickened peroxygen compound containing compositions

(57) Many aqueous compositions containing a peroxygen compound have a very low viscosity and thus easily run off non-horizontal surfaces. Particularly when the peroxygen compound is a soluble peracid, the compositions are difficult to thicken successfully, because many commonly available thickening systems for aqueous media either fail to thicken them or are decomposed and/or decompose the peroxygen compound substantially during storage.

The peroxy compositions, preferably those containing a soluble peracid, are thickened with a thickener system comprising a *dinonylphenolethoxylate* of EO (number of ethylene oxide units) from 4 to 8 in conjunction with a *micelle-forming co-surfactant*. A preferred cosurfactant comprises an amine oxide or a mixture of an alcohol ethoxylate and a polyether. Preferred peracid solutions include dilute equilibrated peracetic acid solutions.

The solutions, when thickened to form a viscous liquid, are suitable for disinfecting and cleaning hard surfaces and when thickened to form a gel are suitable for suspension in an aqueous medium, for example in block form.

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Thickened Peracid Compositions

The present invention relates to thickened compositions and particularly to thickened peroxygen compositions.

During recent years, increasing attention has been paid
5 by industry and the general public in Western Europe and North America to the environmental effects of the many substances that are employed in modern life. One of the classes of substances which have hitherto been widely employed comprises chlorine and oxychlorine derivatives
10 thereof. Such compounds have been reported to generate under appropriate circumstances carcinogenic compounds and as a result, industry is seeking alternatives or replacements for such compounds in order to allay any residual public anxiety.

15 An alternative class of compounds comprises peroxygen compounds, of which one sub-class of especial interest comprises peracids which contain the moiety -CO-OOH . Peracids like hydrogen peroxide enjoy the substantial advantage of generating oxygen, either as such or in an
20 active form during its deployment rather than chlorine or active chlorine species upon which environmentalists currently cast doubts. Furthermore, for a range of purposes such as disinfection, oxidation and bleaching, many of which are encountered domestically, peracids are more effective in
25 general than hydrogen peroxide.

A number of the peracids are either liquid themselves or are produced conveniently in aqueous solution. Although

such compositions are particularly appropriate for the treatment of or incorporation in liquid media, they are less appropriate for the treatment of solid surfaces, and particularly non-horizontal surfaces on account of the ability of liquid compositions to flow away from the point of contact. In consequence, and in order to extend the range of applications for peracids, it would be desirable to devise peracid-containing compositions that flowed less freely.

In principle, liquid compositions can be rendered less free-flowing by the incorporation of materials which thicken the liquid or introduce structure into the liquid. However, it is not impractical to expect that substances which have hitherto been effective thickeners for other liquids would automatically be suitable for thickening liquid peracids or peracid solutions. This difficulty derives from the very same properties of the peracids that make them effective oxidising agents and bleaches. Interaction with thickeners during storage can result in the mutual decomposition of the peracid and the thickener, which in turn not only negates the beneficial effects of thickening, but also progressively removes the capability of the peracid to perform its desired task. It will be recognised that the problem is especially apparent in the case of peracids which are themselves either liquid or are present in solution. There is also a second important difficulty in attempting to thicken peracid solutions. The presence of the peracid and the corresponding carboxylic acid from which it can be derived, tends to significantly inhibit thickening. It is believed that the difficulty arises from interference of the peracid and/or carboxylic acid with aqueous structuring mechanisms which enable surfactants and like materials to thicken aqueous solutions. However, it will be understood that the instant invention does not depend upon the accuracy of the foregoing belief or explanation, but instead it relies upon the results actually demonstrated.

By comparison with soluble peracids, the problem can be somewhat diminished in the case of substantially insoluble solid peracids that are suspended in particulate form in aqueous media, because the peracid and the liquid constitute
5 different physical phases that consequently minimise the extent of chemical interaction between them, and the thickening of the aqueous phase can occur with a lessened risk of interference from dissolved peracid species.

It will be understood that some other potential
10 thickeners may initially or after a brief period of storage produce a much thickened composition, but one which is rather unstable, in that its viscosity falls away rapidly from its peak. Tests employing anionic polyacrylamides fell into that category.

15 It is an object of the present invention to seek to identify thickening substances which capable of thickening peroxygen compositions. It is a second object of some preferred embodiments to identify materials capable of thickening soluble peracid compositions and obtain thereby
20 compositions which are relatively stable during storage. It is a third object of a further set of embodiments of the present invention to identify materials which can thicken peroxygen compositions to produce viscous compositions which can be applied for disinfecting and/or cleansing purposes to
25 non-horizontal surfaces.

According to the present invention there are provided aqueous compositions comprising a soluble peracid in solution together with a thickener characterised in that the thickener comprises a dinonylphenolethoxylate of EO from 4
30 to 8 in conjunction with a micelle-forming co-surfactant and in an amount sufficient to increase the viscosity to at least 100cPs.

By the use of a thickening system of the present invention it is possible to obtain solutions which are
35 thickened and in which the peroxygen compound decomposes by not more than an acceptable extent during storage. In other

words, the composition enjoys both physical and chemical stability.

The invention thickening system is intended particularly for thickening soluble peracids. However, it will be
5 recognised that the thickening system may alternatively be employed to thicken alternative peroxygen compositions, including compositions which are easier to thicken than soluble peracid compositions. In many embodiments, the peroxygen compound is organic. Thus, for example, the
10 system is applicable to organic peroxides, ie organic compounds containing a -C-O-O-H or C-O-O-C- moiety, including alkyl, cycloalkyl or aryl peroxides, acyl peroxides, peroxycarbonates, and organic hydroperoxides and to compositions containing less or even poorly soluble
15 peroxacids such as those containing at least 8 carbons.

In particular, though, the system is applied to compositions containing soluble peracids, which may include low molecular weight aliphatic peroxyacids, for example containing up to 6 carbon atoms, of which especially
20 preferred examples comprise peracetic acid and perpropionic acid. Other examples include perbutyric acid, persuccinic acid and perglutaric acid. The compositions may alternatively include soluble aromatic peroxyacids, such as monoperphthalic acid, or sulphoperbenzoic acid. A mixture
25 of peracids may be employed, if desired.

The peroxygen compound, such as the peracid, may be present in a wide range of concentrations, for example up to about 40%. For any component, % herein is by weight based on the total weight of the composition, unless specifically
30 stated otherwise. The lower limit is at the discretion of the user, but is normally not below about 0.1%. The invention is particularly applicable to ready to use compositions containing a low concentration of active peroxygen compound, and for example compositions intended
35 for application for cleansing and/or disinfecting purposes to hard surfaces and particularly to non-horizontal surfaces. Such dilute compositions typically contain from

0.25 to about 5% by weight of an organic peroxygen compound, preferably a peracid, for example peracetic acid and in a number of practical embodiments the peroxygen compound content will be from about 0.5 to 2%. It will be

5 recognised that such compositions may contain a significant concentration of hydrogen peroxide, which may, for example, comprise from about 1 to 12% of the composition, and in a number of embodiments from 3 to 10%.

The peracid compositions, and particularly those
10 containing aliphatic peracids are often conveniently derived by oxidation of the corresponding aliphatic carboxylic acid with aqueous hydrogen peroxide, and will often contain residual amounts of both the carboxylic acid and hydrogen peroxide. Thus, the compositions may contain up to 40% of
15 the corresponding carboxylic acid and up to 40 % hydrogen peroxide, with a minimum water content usually of 20%. However, in dilute peracid solutions, the concentration of the carboxylic acid and of hydrogen peroxide each tend to be selected in the range from about 1 to 12%. The total
20 concentration of carboxylic acid plus percarboxylic acid is often from 3 to 15%. It is often convenient to restrict the concentration of hydrogen peroxide to no greater than 7%. In many preferred compositions, equilibrium amounts of carboxylic acid, percarboxylic acid and hydrogen peroxide
25 are present.

The thickening system of the present invention comprises a combination of a selected range of phenol ethoxylates, otherwise referred to herein as DNPE and a co-surfactant. By selecting the number of ethylene oxide units in the DNPE
30 within the range of 4 to 8, it has been possible to obtain a level of thickening and viscosity stability which was not observed when using related ethoxylates containing a different number of ethylene oxide units. It will be recognised that DNPE surfactants contain two hydrophobic
35 chains which may contribute to the success of the instant invention in thickening aqueous media that contain significant concentrations of peracid and/or carboxylic

acid, which the investigation leading to the instant invention showed to interfere with thickening by surfactants. However, it is believed that the presence of two such chains is not in itself sufficient, in that some
5 other surfactants containing two such chains have proven not to be as effective at thickening as DNPE.

The amount of DNPE thickener to employ is generally selected in accordance with the proportion of peracid plus carboxylic acid in the composition as well as taking into
10 account the extent of thickening desired. It is desirable to select the concentration of DNPE in the range of from about 2.5 to 15%, and in many instances thickening of dilute peracid compositions can be achieved with quite small amounts of DNPE, such as from about 3 to about 6%.

15 The co-surfactant is conveniently selected from amine oxides, alcohol ethoxylates, polyethers and mixtures thereof. The co-surfactants are normally selected in the range of from about 0.5 to 10% and to some extent, the amount selected depends upon the chemical nature of the co-
20 surfactant. An amine oxide tends to be selected towards the lower end of the range, for example from about 0.5 to about 4%. The amine oxide suitably contains from 14 to 24 carbons, including at least one long chain group, for example containing from 10 to 18 carbons and the remainder
25 comprise short chain alkyl groups such as methyl, ethyl or propyl or hydroxyl substituted alkyl groups such as hydroxyethyl. The alcohol ethoxylate and polyether are each conveniently selected in the range of from 0.5 to 5% and are preferably used together, especially in a total
30 amount of from about 1.5 to 4%. The alcohol ethoxylate suitably contains an alkyl moiety of at least 10 carbons, such as from 12 to 18 carbons and the number of ethylene oxide units is desirably up to about 20, such as from 1 to 15. The polyether can be employed most conveniently in the
35 form of commercial compositions containing a suitable alcohol ethoxylate, such as certain formulations available

under the Trademark LUTENSOL from BASF, such as their grade ES9914.

By suitable choice of thickener system in the preferred amounts, it is possible to obtain peracid compositions
 5 having a viscosity in the region of about 300 to 500cps. Such compositions are advantageous in that they are sufficiently viscous to inhibit movement of thin layers adhering to non-horizontal surfaces, but are sufficiently fluid to enable them to be poured from bulk containers or to
 10 be ejected under pressure through nozzles.

It will be understood that the thickened compositions of the present invention tend to thicken over a period of time, rather than attain the maximum thickness quickly. Advantageously, this means that the compositions normally
 15 still be readily handled using conventional bottling or liquid transporting equipment for a reasonable period after introduction of the thickening system.

The compositions may include one or more stabilisers for peracids and/or hydrogen peroxide so as to encourage the
 20 chemical stability of the thickened products. Known stabilisers for peroxy compounds include aminopolycarboxylic acids, such as EDTA and DTPA, or N-heterocyclic aromatic carboxylic acids such as quinolinic acid, picolinic acid and dipicolinic acid. Particularly effective stabilisers
 25 comprise organic polyphosphonic acids, including hydroxyethylidene-diphosphonic acid and aminopolymethylene phosphonic acids. The latter often satisfy the general formula:

$$X_2N-(-CHR-CHR-NX-)_n-NX_2$$
 in which X represents $-CH_2-PO_3H_2$
 30 R represents H or the two R substituents combine to complete a cyclohexane ring, and n is an integer from 1 to 3. Examples of the formula include ethylenediaminetetra-(methylene phosphonic acid), diethylenetriaminepenta-(methylene phosphonic acid) and cyclohexanediaminetetra-
 35 (methylene phosphonic acid).

In addition to the foregoing components, the composition may also contain one or more perfumes and/or dyes,

preferably selected at least partly on the basis of resistance to oxidation.

The compositions of the present invention can be made by introducing the selected amount of each component in the thickening system into the aqueous solution of peracid and any residual amounts of the corresponding carboxylic acid and hydrogen peroxide, and agitating the mixture to distribute the components substantially evenly through the mixture. This can be conducted at any convenient temperature, for example at the prevailing ambient temperature which is typically in the range of from 10 to 35°C. Alternatively, the mixture may be gently heated to not higher than about 50°C so as to encourage rapid distribution of the components and the mixture thereafter permitted to cool to ambient.

Some of the compositions of the present invention, and particularly those having a viscosity in the region of about 200 to 600cPs are intended for application domestically to surfaces, such as non-horizontal surfaces, which it is desired to disinfect and clean, thereby taking advantage of the disinfectant properties of the peroxygen compound, especially the peracid and the cleansing properties of the detergents. The peroxygen compositions when they have very high viscosities can be regarded as solids, and as such may be incorporated in particulate or granular washing or disinfecting compositions or dispersed in blocks or bars. Such blocks or bars may also incorporate substances such as waxes, either natural or synthetic polymers or very poorly soluble aliphatic carboxylic acids or poorly soluble derivatives and/or mixtures thereof which can regulate and retard the extent of contact between the peroxygen compound composition and for example a liquid medium such as flushing toilet water.

Accordingly, a second aspect of the present invention comprises the use the aforementioned inventioned compositions for disinfecting and cleansing by applying the

composition to a hard surface and permitting contact to be maintained until at least some disinfection has occurred.

The invention compositions may be applied using conventional means and will also take into account the physical state of the composition, particularly whether it is a viscous pourable liquid or a gel. Thus, in its simplest, the compositions may be poured or smeared onto a distributor such as a cloth or sponge and applied to a receiving surface by passage of distributor across the surface. Alternatively, the compositions which have a sufficiently low viscosity for them to be pourable, may be forced through a distributing nozzle directly onto the receiving surface, for example by squeezing a resilient deformable storage container. Compositions in gel form may be applied by a spatula or like article or as indicated previously by incorporation in a host composition or block.

The surfaces onto which the compositions may be applied are often domestic and especially in the kitchen and other locations in which micro-organisms may be found. Suitable receptive surfaces are usually made from wood, glass, ceramics, plastic laminates and metal, and include work surfaces, sinks, pipework, walls, floors, and especially toilet bowls. It will be recognised, though, that similar potentially infected surfaces may be found in non-domestic situations, such as in commercial kitchens, food processing apparatus or containers or brewery or distillery vessels or hospitals or in animal or poultry-rearing establishments or in glass houses or other areas where the maintenance of hygienic conditions is important. The present invention includes the use of invention compositions in such non-domestic situations.

The compositions may subsequently be removed from the surfaces by water washing, possibly applied using a cloth, sponge or like article.

Having described the invention in general terms, specific embodiments thereof will now be described in greater detail by way of example only.

Example 1

In this Example, a thickened peracetic acid solution was made by stirring for a few minutes dinonylphenolethoxylate (EO = 7) available from GAF Corporation under the Trademark ANTAROX grade DM430 in an amount of 4.95%, a cocodihydroxy-ethylamine oxide available from Akzo under their Trademark AROMOX grade C12W in an amount of 1.5% at ambient temperature of about 22°C into an aqueous solution containing 1% peracetic acid, 7% hydrogen peroxide and 9% acetic acid. The viscosity of the composition was measured by a Brookfield viscometer, using spindle no 4 at 10rpm as 360cps. The composition was stored in a polyethylene container and held at ambient temperature in a laboratory storeroom. After 12 weeks, the viscosity of the composition was measured in the same way and a reading of 340 cps was obtained. The chemical stability of the composition was measured by measuring the peracid concentration in the composition before and after the 12 weeks storage by the standard technique employing ceric sulphate/sodium iodide-sodium thiosulphate. It was found that the amount of peracid was the same at the end as at the start of the storage, indicating that no detectable amount of decomposition of the peracid had occurred.

From the results obtained in Exmple 1, it can be deduced that the thickening system employed therein is effective in not only thickening the solubler peracid composition, but is also capable of maintaining both physical and chemical storage stability of the composition during the expected shelf-life of a disinfectant for the domestic market.

When each component of the thickening system is employed alone, no significant thickening of the composition is observed.

Example 2 (present by way of comparison only)

Example 1' was repeated, but employing ANTAROX grade DM 530 a dinonylphenolethoxylate in which EO number was 9 instead of ANTAROX grade DM430. The resultant composition was still thin and very runny, having a viscosity

significantly below 100. The comparison of this result with that obtained in Example 1 demonstrates the importance of selecting a diphenolethoxylate having the correct EO number.

5 Example 3

In this Example, Example 1 was repeated, but employing a dinonylphenol ethoxylate (EO = 5) available from Lanstar grade DNP-5 instead of ANTAROX grade DM430. The viscosity of the composition was 520cps on manufacture and 280cps
10 after 5 weeks storage. Its peracid content at the end of the storage period was still 93% of the starting amount.

From this Example it can be deduced that the use of a dinonylphenolethoxylate in which EO = 5 is also acceptable.

Example 4

15 In this Example, Example 3 was repeated, but employing a different amine oxide, namely AROMOX grade DM14DW, which was dimethyltetradecylamine oxide instead of AROMOX C12W. The composition had an initial viscosity of 680 cps, rising to 800cps after 5 weeks storage and the residual peracid
20 content was 95% at the end of the storage period. This Example demonstrates that the alternative amine oxide is very effective in conjunction with the suitably selected dinonylphenolethoxylate at thickening peracid compositions stably.

25 Example 5

In this Example, Example 1 was repeated, but with a change to both the dinonylphenolethoxylate and amine oxide. The former was obtained from Lanstar, grade DNP-7, EO = 7, ie a different source of the same material, and the co-
30 surfactant comprised 2.5% of a mixture of a fatty alcohol ethoxylate and a polyether obtainable from BASF under their Trademark LUTENSOL grade ES 9914. The composition had an initial viscosity of 280cps and after 12 weeks storage had a viscosity that had apparently fallen to 180cps. 90% of its
35 peracid content had been retained during storage. If double the concentration of both the Lanstar and LUTENSOL surfactants were employed, a composition having an initial

viscosity of 8000cps was obtained, rising to over 14000cps after 12 weeks storage. The results obtained in this Example indicate that a stable thickened composition can be obtained using the two surfactants employed therein, though possibly for preference in amounts that are intermediate
5 between the levels tested.

CLAIMS:-

1. Aqueous compositions comprising a peroxygen compound at least partly in solution together with a thickener characterised in that the thickener system comprises a dinonylphenolethoxylate of EO from 4 to 8 in conjunction with a micelle-forming co-surfactant and in an amount sufficient to increase the viscosity to at least 100cPs.
2. A thickened composition according to claim 1 characterised in that the peroxygen compound is a peracid.
3. A thickened composition according to claim 2 characterised in that the peracid is soluble.
4. A thickened composition according to claim 3 characterised in that the peracid is peracetic acid.
5. A thickened composition according to any preceding claim characterised in that it contains from 0.25 to 5% w/w peracid.
6. A thickened composition according to any preceding claim characterised in that it contains amounts of a carboxylic acid and hydrogen peroxide each selected in the range of from about 1 to 12% w/w.
7. A thickened composition according to claim 6 characterised in that the combined proportions of peracid and carboxylic acid is in the range of from 3 to 15%.
8. A thickened composition according to any preceding claim characterised in that the amount of phenol ethoxylate thickener employed is selected in the range of from 2.5 to 15%, preferably 3 to 6% w/w of the composition.

9. A thickened composition according to any preceding claim characterised in that it contains from about 0.5% to 10% of a co-surfactant selected from amine oxides, alcohol ethoxylates and polyethers.
10. A thickened composition according to claim 9 characterised in that it contains from 0.5 to about 4% amine oxide.
11. A thickened composition according to claim 9 characterised in that the composition contains from 1.5 to 4% in total of an alcohol ethoxylate and a polyether.
12. A process for preparing a thickened composition by introducing an effective amount of a dinonylphenol-ethoxylate of EO from 4 to 8 in conjunction with a micelle-forming co-surfactant into an aqueous composition containing a peroxygen compound and agitating the mixture.
13. A process according to claim 12 characterised in that it employs one or more of the characterising features of claims 2 to 11.
14. Use of a thickened peroxygen composition according to any of claims 1 to 11 or produced by the process of claim 12 or 13 as a disinfectant.
15. A thickened peroxygen composition or a process for making a thickened peroxygen composition or the use of a thickened composition as a disinfectant substantially as described herein with respect to any novel feature or novel combination of features.

Examiner's report to the Comptroller under
Section 17 (The Search Report)

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Relevant Technical fields

(i) UK CI (Edition K) A5E (ET); C5D (DEB, DFB, DHX)

(ii) Int CL (Edition 5) A01N; C11D

Search Examiner

S J QUICK

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASE: WPI

Date of Search

5 JUNE 1992

Documents considered relevant following a search in respect of claims

1-14

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	EP 0125781 A1 (INTEROX CHEMICALS LTD) - see pages 15 (lines 6-8), 35, 37-39 41 and 45 and especially example 43 (table 7, page 41)	1 at least
A	US 4557898 A (STERLING DRUG INC) - see Column 3 (lines 4-7) and Examples 1 (Column 4, lines 50-65) and 5 (Column 14, lines 25-38)	
A	US 4547306 A (HENKEL KGaA) - see Example 6 (table I, Column 10)	

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family, corresponding document.

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